

PATENT SPECIFICATION

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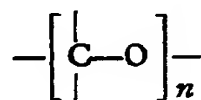
COMPLETE SPECIFICATION

Process for Stabilising Macromolecular Polyacetals

We, CHEMISCHE WERKE HÜLS AKTIEN-GESELLSCHAFT, a German Company, of 4370 Marl, Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

This invention relates to a process for stabilising macromolecular polyacetals against oxidative and thermooxidative degradation.

Throughout the specification, polyacetals are defined as polymers having the fundamental units:



the carbon atom having attached to it preferably two hydrogen atoms or otherwise one hydrogen atom and an alkyl radical, which may also bear substituents. These polyacetals may be prepared by various methods. Highly purified monomeric formaldehyde may be polymerised in the presence of anionic or cationic catalysts in inert solvents or in the gas phase. On the other hand it is possible to obtain corresponding polyoxymethylenes having high molecular weight and good thermostability by polymerisation of 1,3,5-trioxane by means of cationic initiation or the action of ionising radiation. Higher aldehydes, for example acetaldehyde or propionaldehyde, will form polyacetals. They also include polymers which have been obtained by copolymerisation of aldehydes or cyclic acetals such as trioxane and in which the polymer chains contain either groupings as well as the acetal compounds. Examples of suitable comonomers are oxacyclic compounds containing at least two vicinal carbon atoms, prepolymers prepared from oxacyclic compounds and cationically polymerisable vinyl compounds. Finally some of the oxygen atoms in the polyacetal chain may be replaced by sulphur atoms.

[Price 5s. 0d.]

The polyacetals obtained by polymerisation contain terminal hydroxyl groups, decomposed when heated and therefore have to be stabilised by esterification or etherification of the terminal hydroxyl groups. In the case of ether groupings in the polymer chain, the ends of the chains may also be degraded by suitable means up to the nearest ether grouping, further thermal degradation being impossible beyond this point.

In the heat which particularly occurs in the processing of polyacetals in the conventional processing machines for thermoplastics, polyacetals having stabilised terminal groups are however also more or less unstable and tend to depolymerisation and chain cleavage, so that monomeric aldehydes and their secondary products are formed.

It is known that polyacetals may be stabilised against the action of heat by adding compounds which are capable of intercepting the aldehydes and their secondary products formed by thermal cleavage, of blocking active centres occurring in the polymers and of preventing depolymerisation. For example the addition of hydrazine derivatives, urea derivatives, thio-urea derivatives, dicarboxylic acid diamides, amides of polybasic aromatic sulphonic acids, polymerised amides or polymers of N-vinyl-lactams has proved to be effective in this respect (USA Patent Specification No. 2,296,249, German Printed Application No. 1,066,739).

Polyacetals are however even more unstable to the simultaneous action of oxygen and heat, which makes necessary the additional incorporation of antioxidants. The stabilisers hitherto proposed against this oxidative degradation are amines, organic compounds having sulphur atoms and nitrogen atoms in the molecule (German Patent Specification No. 1,076,363), and also phenols of which polynuclear phenolic antioxidants have hitherto been regarded as the most effective.

Many of the phenolic stabilisers, however, although they give good protection against the attack of oxygen, cause considerable change in colour of the polyacetals protected by them.

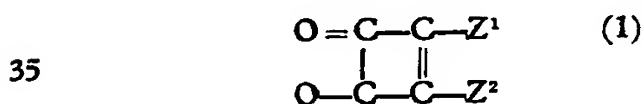
- 5 The polyacetals quickly becomes yellow brown, dark brown or even black after they have been exposed to the atmosphere or sunlight. Moreover many of the phenolic compounds volatiles by reason of the high vapour pressure or good sublimability in the range of processing temperatures of 150° to 230°C and consequently result in a decreased stability of the polymers.

- 10 Known compounds of the benzophenone and cinnamionitrile types which absorb in the ultra-violet range have been proposed as stabilisers against light.

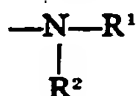
- 15 In principle it is of high industrial interest to further improve the stabilisation of polyacetals because (a) processing is facilitated and (b) range of use is widened. Moreover as soon as thermally stable mixtures exist, polyacetals which soften at high temperature may be processed with higher degrees of polymerisation so that such polymers which are even more valuable mechanically are made accessible.

The invention has for its object a further perfection of stabilisation.

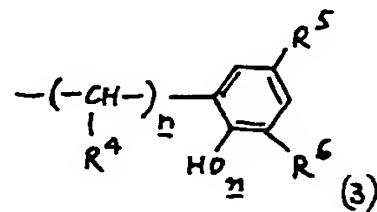
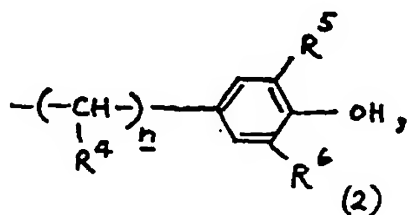
- 20 This object is achieved in accordance with this invention by adding to the polyacetal, if desired in combination with one or more thermostabilisers and/or other antioxidants, in a concentration of 0.001 to 10% by weight (based on the polyacetal) an unsaturated compound having the general formula (1):—



wherein Z^1 and Z^2 , which may be identical or different, denote the group



- 40 or the group $-\text{O}-\text{R}^3$ in which R^1 and R^2 , which may be identical or different, each denote a hydrogen atom, a linear, branched or cyclic alkyl radical, or a hydroxyalkyl, alkenyl, aralkyl, aryl, nitroaryl, alkoxyaryl or dialkylaminoaryl radical, any of which radicals may if desired bear a heterocyclic substituent, or a radical having the general formula (2) or (3):—

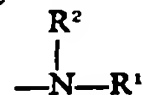


in which n denotes zero or 1 and R^4 , R^5 and R^6 , which may be identical or different, each denote a hydrogen atom, a linear or branched alkyl radical, or a



50 radical (in which R^7 denotes a hydrogen atom or an acyl radical of an aliphatic carboxylic acid having one to five carbon atoms), or R^1 and R^2 together with the nitrogen to which they are attached denote a heterocycle which may contain oxygen or sulphur as further hetero atoms in addition to the nitrogen, and R^3 denotes a hydrogen atom or a linear, branched or cyclic alkyl radical.

Examples of suitable compounds in which Z^1 and Z^2 denote



and R^1 and R^2 each denote a hydrogen atom, a linear, branched or cyclic alkyl radical, or a hydroxyalkyl, alkenyl, aralkyl, aryl, nitroaryl, alkoxyaryl or dialkylaminoaryl radical, any of which may bear a heterocyclic substituent, are:

- Diaminocyclobutenedione,
N - methyldiaminocyclobutenedione,
N - methyl - N' - ethyldiaminocyclobutenedione,
N,N' - di - n - butyldiaminocyclobutenedione,
N,N' - dilauryldiaminocyclobutenedione,
N - butyl - (2) - diaminocyclobutenedione,
N,N' - bis - (2 - ethylhexyl) - diaminocyclobutenedione,
N,N' - dicyclohexyldiaminocyclobutenedione,
N,N' - bis - (3 - methyl - butene - (2) - yl - (1)) - diaminocyclobutenedione,
N - ethyl - N' - benzyldiaminocyclobutenedione,
N,N' - dibenzyldiaminocyclobutenedione,
N,N' - diphenyldiaminocyclobutenedione,
N,N' - dinaphthyl - (1) - diaminocyclobutenedione,
N - hydroxyethyl - N' - lauryldiaminocyclobutenedione,
N,N' - bis - (hydroxyethyl) - diaminocyclobutenedione,

- N,N' - bis - (1 - hydroxymethyl) - n-propyl) - diaminocyclobutenedione,
 N,N' - bis - (3 - hydroxypropyl) - diaminocyclobutenedione,
 5 N,N' - bis - (p - nitrophenyl) - diaminocyclobutenedione,
 N,N' - bis - (o - methoxyphenyl) - diaminocyclobutenedione,
 N,N' - bis - (4 - dimethylaminophenyl) - diaminocyclobutenedione,
 10 N,N,N',N' - tetraethyldiaminocyclobutenedione and
 N,N,N',N' - tetra - n - butyldiaminocyclobutenedione.
- 15 Examples of suitable compounds in which Z¹ and Z² denote —O—R³ are:
 dimethoxycyclobutenedione and dicyclohexylcyclobutenedione diether.
- 20 Examples of suitable compounds in which Z¹ and Z² are different are:
 1 - amino - 2 - ethoxycyclobutenedione,
 1 - laurylamino - 2 - ethoxycyclobutenedione, and
 1 - phenylamino - 2 - butoxycyclobutenedione.
- 25 Examples of compounds in which R¹ and R² denote radicals having the general formulae (2) and (3) above in which n denotes zero or 1 and R⁴, R⁵ and R⁶ are identical or different and denote hydrogen atoms, linear or branched alkyl radicals are:
 30 N,N' - bis - (p - hydroxyphenyl) - diaminocyclobutenedione,
 N,N' - bis - (3 - methyl - 4 - hydroxyphenyl) - diaminocyclobutenedione,
 35 N,N' - bis - (3,5 - dimethyl - 4 - hydroxyphenyl) - diaminocyclobutenedione,
 N,N' - bis - (3 - methyl - 4 - hydroxy - 5 - tert - butylphenyl) - diaminocyclobutenedione,
 40 N,N' - bis - (o - hydroxyphenyl) - diaminocyclobutenedione,
 N,N' - bis - (2 - hydroxy - 3 - tert - butylphenyl) - diaminocyclobutenedione,
 45 N,N' - bis - (2 - hydroxy - 3 - methyl - 5 - tert - butylphenyl) - diaminocyclobutenedione,
 N,N' - bis - (p - hydroxybenzyl) - diaminocyclobutenedione,
 50 N,N' - bis - (3 - methyl - 4 - hydroxybenzyl) - diaminocyclobutenedione,
 N,N' - bis - (2 - hydroxy - 3 - methyl - 5 - tert - butylphenyl) - diaminocyclobutenedione,
 55 N,N' - bis(1 - (3 - methyl - 4 - hydroxyphenyl) - ethyl) - diaminocyclobutenedione and
 N,N' - bis - (1 - (2 - hydroxy - 5 - tert - butylphenyl) - butyl) - diaminocyclobutenedione.
- Examples of suitable compounds in which R¹ and R² denote
- $$\begin{array}{c}
 \text{—C—N—H} \\
 || \quad | \\
 \text{O} \quad \text{R}^7
 \end{array}$$
- in which R⁷ denotes a hydrogen atom or an acyl radical of an aliphatic carboxylic acid having one to five carbon atoms are:
- di-ureidocyclobutenedione,
 bis-(N-acetyluroido)-cyclobutenedione or
 bis-(N-caproyluroido)-cyclobutenedione.
- Examples of compounds in which R¹ and R² form heterocycles with the nitrogen and which may contain oxygen or sulphur as heteroatoms as well as nitrogen are:
- dipyrrolidinocyclobutenedione,
 dimorpholinocyclobutenedione,
 1-pyrrolidino-2-ethoxycyclobutenedione and
 1-morpholino-2-butoxycyclobutenedione.
- Possibilities for the synthesis of these compounds are described by G. Maahs in Liebigs Ann. Chem. 686 (1065) 55 and by G. Maahs and P. Hegenberg in Angew. Chem., 78, 927—931 (1966).
- The following are examples of compounds which have proved to be particularly effective:
- diaminocyclobutenedione,
 N,N' - di - n - butyldiaminocyclobutenedione,
 N,N' - dibutyl - (2) - diaminocyclobutenedione,
 N,N' - di - tert - butyldiaminocyclobutenedione,
 N,N' - dilauryldiaminocyclobutenedione,
 N,N' - diphenyldiaminocyclobutenedione,
 N,N' - bis - (p - hydroxyphenyl) - diaminocyclobutenedione,
 N,N' - dicyclohexyldiaminocyclobutenedione,
 dimorpholinocyclobutenedione,
 dipyrrolidinocyclobutenedione,
 N,N,N',N' tetra - n - butyldiaminocyclobutenedione,
 N - hydroxyethyl - N' - lauryldiaminocyclobutenedione,
 1 - amino - 2 - ethoxycyclobutenedione,
 1 - laurylamino - 2 - ethoxycyclobutenedione,
 1 - phenylamino - 2 - ethoxycyclobutenedione,
 1 - pyrrolidino - 2 - ethoxycyclobutenedione,
 diethoxycyclobutenedione and
 dibutoxycyclobutenedione.

These antioxidants are added to the polymer in 0.001 to 10% by weight, preferably 0.1 to 5% by weight. The effectiveness of these compounds may be increased by adding 0.01 to 10% by weight, preferably 0.1 to 5% by weight, based on the polyacetal, of a thermo-stabiliser. Examples of suitable thermo-stabilisers are urea derivatives, dicarboxylic diamides or polyamides. A combination of these stabilisers having different actions is synergistic.

The stabilisers may be mixed with the high molecular weight polyacetals by known methods before or during the processing. For example the finely powdered stabiliser may be incorporated into the polyacetal in a mixer or a solution of the stabiliser in a solvent may be absorbed on the polymer while stirring and freed from solvent in a stream of hot nitrogen while stirring. On the other hand the stabiliser and polyacetal may be suspended in a solvent and the solvent then removed. Furthermore the said stabilisers may be incorporated into the polymers by kneading or rolling in the melt.

If desired, the polyacetals may also have other additives, such as plasticisers and pigments, incorporated therein as well.

The stability of the polyacetals stabilised with the stabilisers to be used according to this invention is determined by the so-called volatile number (VN). Volatile number is the loss in weight in per cent which a 200 mg sample undergoes when it is heated in a glass tube of the dimensions 14 x 50 mm under the action of air at 220°C, VN₂₀ being the loss in weight per cent after twenty minutes and VN₄₀ being the loss in weight per cent between twenty and forty minutes.

The viscosity data given are measured in solutions of the polymers in dimethylformamide and at a concentration of 0.25 g/100 ml at a temperature of 135°C in the presence of diphenylamine (1 g/100 ml). The results of this determination are expressed by the reduced viscosity (RV) which is defined as follows:

$$\text{reduced viscosity} = \frac{\text{specific viscosity}}{C}$$

where C is the concentration in g/100 ml of the dissolved substance.

Formaldehyde homopolymers are used in the Examples, such as are obtained according to the process of French Patent Specification No. 1,254,844; the reduced viscosity amounts to at least 3.0. They are acetylated according to the process of British Patent Specification No. 770,717.

Trioxane copolymers are also used in the Examples, and are obtained as follows:

135 g of freshly distilled trioxane having a water content of less than 30 ppm is intimately mixed at 70°C in a glass vessel with 5 mole% of 1,3-dioxacycloheptane and 0.125 ml of a 5% by weight solution of boron trifluoride diethyl etherate in benzene, transferred to a polyethylene bag (10 x 25 cm) and caused to polymerise in a waterbath at 70°C, this requiring three to five minutes. The solid polymer block is broken up, stirred with water, cold and hot ammonium carbonate solution, washed with hot distilled water until neutral and dried overnight at 50°C in a vacuum drying cabinet. Reduced viscosity: 1.0 to 1.5 dl/g.

The invention is illustrated by the following Examples.

EXAMPLE 1

In each case 5 g of trioxane copolymer is ground to dryness with a solution of dispersion of the various stabilisers in an organic solvent in a mortar, solvent is again added and again it is ground to dryness. After the sample has been dried overnight at 50°C in a vacuum drying cabinet, the volatile numbers (VN₂₀ and VN₄₀) are determined. The results (Experiments Nos. 6 to 9) are given in Table I together with comparative experiments (Experiments Nos. 1 to 5 marked with a C). In Table I, E = Experiment No.; %wt. = weight per cent.

TABLE I

E	Stabiliser	%wt	VN ₂₀	VN ₄₀
1C	without stabiliser	—	12.6	9.8
2C	4,4'-methylene-bis-(2,6-di-tert-butylphenol)	0.2	6.7	2.1
3C	2,2'-methylene-bis-(4'-methyl-6-tert-butylphenol)	0.2	6.3	1.5
4C	phenyl-β-naphthylamine	0.2	4.5	1.6
5	1,4-phenylenediamine	0.2	4.3	1.5
6	N,N'-di-n-butyl-diaminocyclobutenedione	0.2	4.8	0.4
7	N,N'-di-tert-butyl-diaminocyclobutenedione	0.2	6.4	1.1
8	N,N'-bis-(p-hydroxyphenyl)-diaminocyclobutenedione	0.2	3.7	0.9
9	N,N'-bis-(p-hydroxyphenyl)-diaminocyclobutenedione	0.4	3.4	0.6

Experiments with N,N'-dilauryldiaminocyclobutadione, N,N'-dihydroxyethyldiaminocyclobutenedione, dipyrrolidinocyclobutenedione, diureidocyclobutenedione, 1-pyrrolidino-2-ethoxycyclobutenedione and dibutoxycyclobutenedione give comparable results.

EXAMPLE 2

In each case 25 g of trioxane copolymer is

mixed according to Example 1 with the stabiliser and treated at 210° to 215°C on an electrically heated roller. Samples are taken off from the roller after certain times and the volatile number thereof is determined. The results are collected in Table II: the superpolyamide is a tercondensate according to patent claim 5 of German Printed Application No. 1,066,739. HT = duration of heat treatment in minutes.

TABLE II

E	Stabiliser	HT	VN ₂₀	VN ₄₀
1C	0.2% of superpolyamide + 0.3% of 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol) (completely decomposed in up to 10 minutes)	0	5.0	0.8
		5	1.6	4.9
2	0.2% of superpolyamide + 0.3% of N,N'-bis-(p-hydroxy-phenyl)-diaminocyclobutenedione	0	4.5	0.5
		5	1.2	1.6
		10	2.0	2.8
		15	2.0	2.3
		20	2.2	3.0

When N,N' - dibutyl - (2) - diaminocyclobutenedione, N,N' - dicyclohexyldiaminocyclobutenedione or N,N' - bis - (3 - methyl - 4 - hydroxy - 5 - tert - butylphenyl) - diaminocyclobutenedione is used instead of N,N' - bis - (p - hydroxyphenyl) - diaminocyclobutenedione, comparable results are obtained.

EXAMPLE 3

In each case 5 g of an acetylated formaldehyde homopolymer is mixed according to Example 1 with the stabilisers. The results are given in Table III.

TABLE III

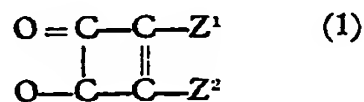
E	Stabiliser	% wt	VN ₂₀	VN ₄₀
1C	without stabiliser	—	24.0	13.6
2C	2,2'-methylene-bis-(4-methyl-6-tert-butyl-phenol)	0.2	15.3	12.9
3	N,N'-bis-(p-hydroxyphenyl)-diaminocyclobutenedione	0.2	5.4	5.9

When N,N' - di-tert-butyl-diaminocyclobutenedione, N,N' - diphenyl-diaminocyclobutenedione, 1-phenylamino-2-ethoxycyclobutenedione or diethoxycyclobutenedione is used instead of N,N' - bis-(p-hydroxyphenyl) - diaminocyclobutenedione the results are comparable.

The advantages achieved with the invention consist particularly in the fact that the power of resistance of the polymers to thermo-oxidative degradation is surprisingly higher than is achieved with prior art stabilisers in the same concentration. As the Examples show, the new stabilisers are also capable of improving quite considerably by admixture the action of stabilisers hitherto considered most efficient, which action in some cases has not been entirely satisfactory. The mixtures stabilised in accordance with this invention are particularly suitable for the production of films, filaments, threads, and moulded articles obtained by extrusion, injection mouldings and other conventional methods. Latitude in processing as regards temperature is wider and the mouldings may therefore be prepared from high molecular weight polyacetals.

WHAT WE CLAIM IS:—

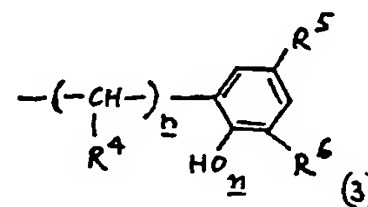
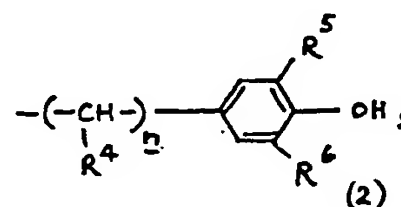
1. A process for stabilising a macromolecular polyacetal as hereinbefore defined against oxidative and thermo-oxidative degradation which comprises adding to the polyacetal, if desired in combination with one or more thermostabilisers and/or other antioxidants, in a concentration of 0.001 to 10% by weight (based on the polyacetal) an unsaturated compound having the general formula (1):—



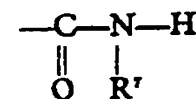
wherein Z¹ and Z², which may be identical or different, denote the group



or the group —O—R³ in which R¹ and R², which may be identical or different, each denote a hydrogen atom, a linear, branched or cyclic alkyl or a hydroxyalkyl, alkenyl aralkyl, aryl, nitroaryl, alkoxyaryl, or dialkyl-amino-aryl radical, any of which radicals may if desired bear a heterocyclic substituent, or a radical having the general formula (2) or (3):—



in which n denotes zero or 1, and R⁴, R⁵ and R⁶ which may be identical or different, each denote a hydrogen atom, a linear or branched alkyl radical or a



radical (in which R⁷ denotes a hydrogen atom or an acyl radical of an aliphatic carboxylic acid having one to five carbon atoms), or R¹ and R² together with the nitrogen to which they are attached denote a heterocycle which may contain oxygen or sulphur as further hetero atoms in addition to the nitrogen, and R³ denotes a hydrogen atom or a linear, branched or cyclic alkyl radical.

2. A process as claimed in claim 1 wherein the amount of the compound having the formula (1) is 0.1 to 5% by weight.

3. A process as claimed in claim 1 or 2 wherein 0.01 to 10% (on the polyacetal) of a thermostabiliser is added. been stabilised by the process claimed in any of claims 1 to 5. 10
- 5 4. A process as claimed in claim 3 wherein the said percentage is 0.1 to 5% by weight.
5. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.
6. Macromolecular polyacetals which have

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